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SEP 76 P E COFFEY, W N STASIUK, V A MOHNEN N00014-76-C-0283

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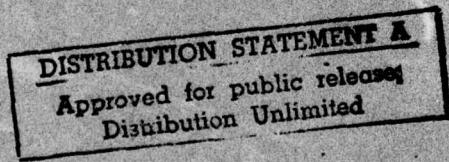


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OZONE IN RURAL AND URBAN AREAS OF NEW YORK STATE



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6 OZONE IN RURAL AND URBAN AREAS OF NEW YORK STATE

PART I

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10 P.E. Coffey, W.N. Stasiuk, V.A. Mohnen

ABSTRACT

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Ozone concentrations have been measured at rural and urban sites in New York State for the last several years. Most of the ozone found at these sites is the resultant of long range transport processes and not local photochemical generation. Periods of high ozone concentrations are regional in nature and are associated with high pressure weather systems. The nitric oxide and particulate matter produced in urban areas destroys ozone and thus these areas tend to experience fewer hours of ozone concentrations in excess of 80 ppb than do the rural areas. However, on occasion, ozone appears to be generated in the urban plume in excess of the prevailing background ozone concentrations. The magnitude of the contribution of ozone so generated to the overall ozone levels in the air mass associated with the high pressure system is both variable and uncertain.

INTRODUCTION

Several years ago, the Division of Air Resources of the New York State Department of Environmental Conservation and the Atmospheric Sciences Research Center of the State University of New York initiated a continuing study designed to investigate the sources of the ozone being found in New York State and the northeastern United States.

Quite frequently, starting in late spring and continuing throughout the summer, ozone concentrations in excess of the National Ambient Air Quality Standard (80 ppb not to be exceeded more than one hour per year) were being recorded at urban monitoring sites in New York State. While these urban sites usually recorded ozone concentration patterns which corresponded to the classical diurnal cycle characteristic of local photochemical generation and subsequent destruction, there was evidence that the problem was more complex. Earlier studies by New York State<sup>(1)</sup> in the mid-1960's, using the cracking of rubber as an indicator of ozone, indicated that ozone concentrations were higher in the rural areas than in the urban areas. These results were reinforced by Johnston<sup>(2)</sup> and Richter<sup>(3)</sup> who, in the early 1970's, measured high concentrations of ozone in rural Maryland and West Virginia, respectively.

STUDY DESIGN

The ozone study was designed to collect and analyze ozone data over a large area from both stationary surface sites and instrumented aircraft. To supplement existing urban monitors situated in the larger cities of New York State, several sites were added.

\* Supported by ONR No. N0001476C0283.

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The summit atmospheric physics laboratory at Whiteface Mountain (Elevation 4,980 feet) in the northern Adirondack Mountains of New York was chosen to be a permanent site. This laboratory, operated by the Atmospheric Sciences Research Center of the State University of New York, is situated in a very remote area of the Northeast well over 100 miles from the nearest sizable urban area. The elevation of the site, which is above the tree line, is sufficient to place it above the summertime nocturnal inversion layer yet low enough so that it remains well within the daytime surface mixing layer.

A temporary rural elevated site was set up in a fire tower 40 feet above the summit of Mount Utsayantha (Elevation 3,200 feet) located in Delaware County approximately 180 miles south of Whiteface Mountain. This site has the same meteorological characteristics as the Whiteface site.

A third temporary rural site was operated in a remote conifer forested valley area known as the "Pack Forest." This site (Elevation 800 feet) was approximately 55 miles south of Whiteface. Unlike the other two rural sites, the Pack Forest location was typically under the nocturnal inversion layer. The location of these rural sites and several urban sites used during the study is shown in Figure 1.

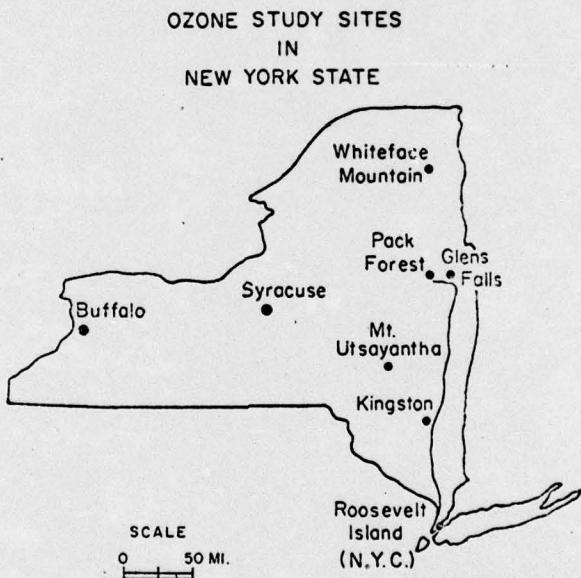


Figure 1. Locations of Various Sites in New York State

In addition to the above mentioned fixed location sites, instrumented helicopter and airplane flights were made on both a local and long-range basis.

## RESULTS

The Whiteface station, because of its isolation from urban areas, produced ozone data which was unperturbed by local anthropogenic sources. The monthly average ozone concentration at this site for 1973 and part of 1974 are shown in Figure 2. The classical springtime rise is evident as is the fall and winter low. While not evident in this figure, the month of highest ozone concentration is very dependent on year by year climate variations. For example, while the 1973 highest average ozone concentrations were measured for August, the highest month in 1974 was June. This coincided with a shift in 1974 climatic conditions producing winter-like weather patterns over the northeastern United States after June of that year.

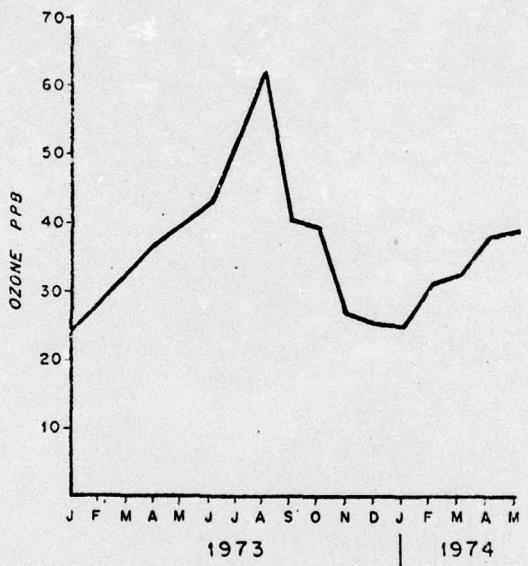


Figure 2. Average Monthly Ozone Concentrations Recorded at Summit of Mount Whiteface

### EFFECT OF NOCTURNAL INVERSION

In Figure 3, ozone concentrations at the Whiteface site are compared with those at the Pack Forest site from August 6, 1973 to August 17, 1973. The Pack Forest valley site, which is under the nocturnal inversion, recorded distinct diurnal variations in ozone concentration which look very much like the classical case of local daytime photochemical ozone generation and subsequent nighttime destruction. However, the lack of local anthropogenic sources and the existence of high concentrations of ozone above the nocturnal inversion layer as seen from the Whiteface data suggests a different mechanism<sup>(4)</sup>. That is, the ozone seen at both sites is generated elsewhere and

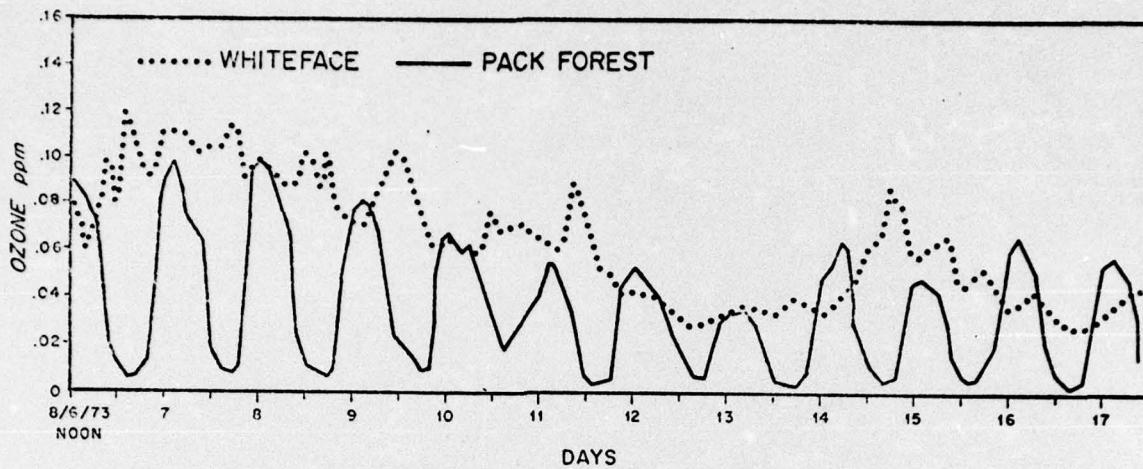


Figure 3. Ozone Concentrations at Whiteface and Pack Forest from August 6, 1973 to August 17, 1973

transported over long distances to these locations. The distinct diurnal variation at the Pack Forest site is caused by local nighttime destruction of ozone under the nocturnal inversion layer by reaction with gases such as nitric oxide and terpenes, by contact with the surface and by reaction with particulate matter. The daytime breakup of the inversion layer allows ozone replenishment from the ozone reservoir above this layer.

That this mechanism is responsible for diurnal ozone fluctuations in urban areas can also be demonstrated.

Approximately 25 miles to the south and east of the Pack Forest is located the city of Glens Falls (population 18,500). Its ozone concentrations are almost identical to those found at the Pack Forest site. The relationship between these two sites is illustrated in Figure 4 on an hourly average basis for the month of July, 1973. Note also on this figure the Whiteface hourly average which exhibits a reverse diurnal. Evidently, the ozone concentration at Whiteface experiences a daytime minimum due to the influx of ozone depleted air from under the nocturnal inversion. During the winter months when the snow covered mountain summit is typically under the nocturnal inversion, the summit ozone diurnal fluxuation is reversed as would be expected.

#### LONG RANGE TRANSPORT

That long range transport of ozone occurs on a massive scale is suggested by Figure 5. In this figure, continuous ozone data from the Whiteface site for the first 17 days of August, 1973 is presented for comparison with the rural Utsayantha site and the urban site of Syracuse, New York. The

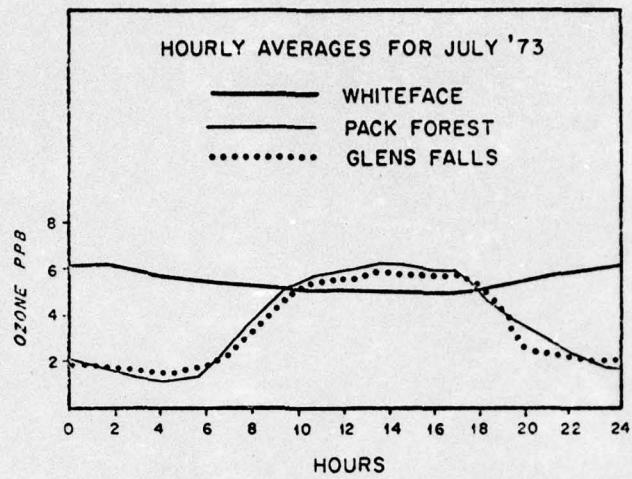


Figure 4. Hourly Ozone Averages at Whiteface, Pack Forest and Glens Fall Sites for July, 1973

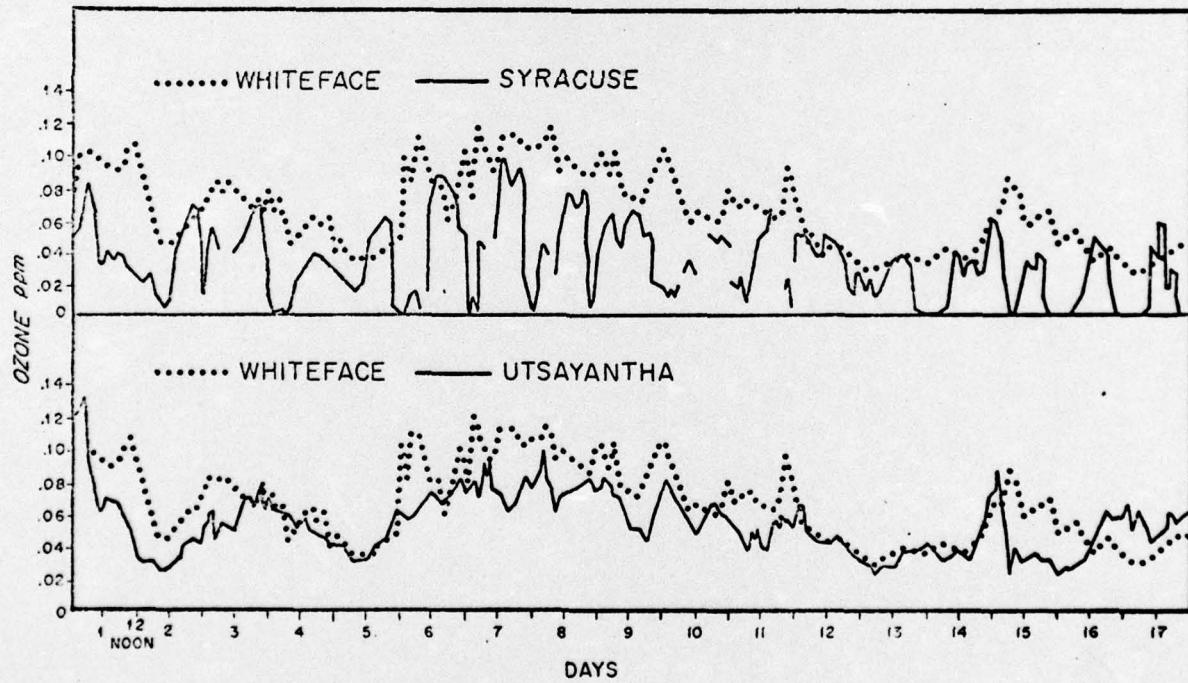


Figure 5. Comparison of Ozone Concentration at Whiteface Site with that at Utsayantha and Syracuse Sites for the First 17 Days of August, 1973

missing ozone data is a result of malfunctions in the data transmission system of the continuous air monitoring network. Despite a separation of 180 miles between the two rural stations (Utsayantha and Whiteface), the ozone levels at both sites are nearly equal and exhibit the same variations.

Of perhaps more interest are the comparisons of the urban ozone concentrations at Syracuse with the rural concentrations at Whiteface. The typical diurnal ozone pattern is seen in the urban areas with nighttime values usually reduced to zero by reaction with nitric oxide. A close examination of this figure shows that the urban daily maximum ozone values apparently are high when non-urban ozone values are high and are low when non-urban values are low. We have reported similar relationships for Whiteface, Glens Falls and Montreal, Canada(5). This strengthens the hypothesis that the urban ozone observed in New York State may be more the resultant of a physical process of transport and mixing than of local photochemical generation.

#### WEATHER

Episodes of high ozone concentrations are associated with high pressure systems. Ozone concentrations rise as the center of the high moves southeast of the area during which time the surface winds blow from the southwest quadrant. Elevated sulfate concentrations are also associated with these systems.(5,6)

#### URBAN OZONE

It has been shown by Coffey and Stasiuk(7) that urban areas experience fewer hours in excess of the 80 ppb ozone standard than do rural areas. Figure 6 illustrates this point for the cities of New York, Mamaroneck, Buffalo, Glens Falls and the rural sites at Whiteface and the Pack Forest. Apparently, the destruction of ozone by nitric oxide tends to be greater than the photochemical generation of ozone within the urban area.

#### URBAN OZONE PLUME

Figure 6 is interesting in that all the sites but one experience ozone maximums of around 135 ppb. The site at Mamaroneck, however, experiences several hours of ozone concentrations significantly higher. This site is approximately 20 miles from New York City and typically downwind during an ozone episode. An explanation of these high ozone concentrations is that on occasion when reaching the Mamaroneck area, the urban plume from the New York City area has depleted its nitric oxide content and has become a net producer of ozone. This argument is reinforced by Figure 7 - an ozone concentration isopleth of the northeastern area drawn from data supplied by 95 ozone reporting stations in the region. Several ozone plumes are evident as is the regional nature of the ozone problem.

#### CONCLUSIONS

The diurnal fluctuations in ozone concentration observed at surface sites is largely the resultant of local meteorological parameters and not

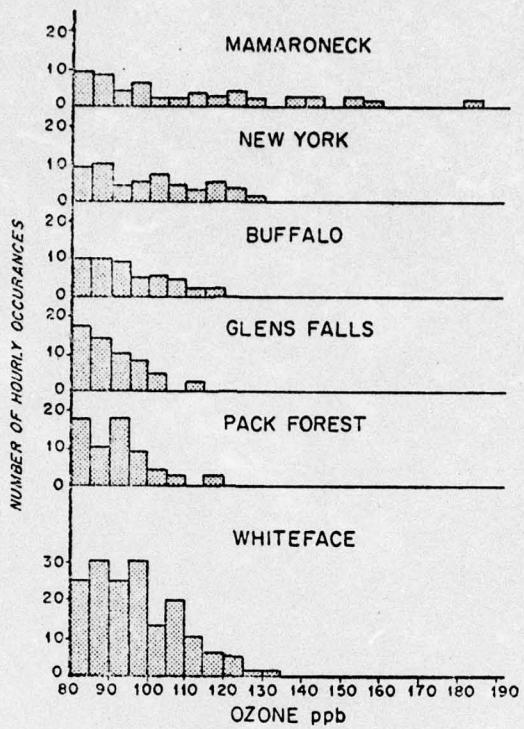


Figure 6. Frequency Distribution of Ozone Concentrations in Excess of 80 ppb from 7/1/73 to 8/22/73

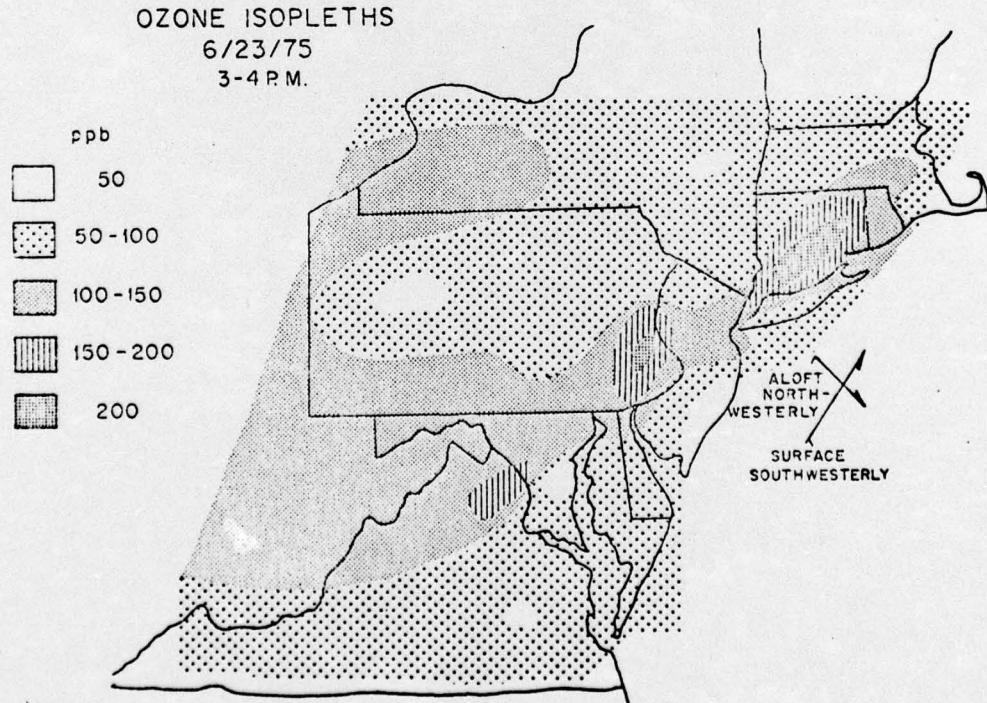


Figure 7. 3-4 P.M. Ozone Concentration Isopleths of Several Northeastern States for June 23, 1975

local photochemical generation. Above the nocturnal inversion ozone a high concentration persists throughout the night and serves to replenish the surface ozone concentrations during the daylight hours.

The ozone problem is a regional one, episodic in nature associated with high pressure systems.

Urban areas tend to have less ozone than do rural areas, however, ozone plumes have been measured downwind of the larger urban areas. The relative contribution of ozone generated in urban plumes to the overall ozone concentrations associated with high pressure systems is unknown. Similarly, the relative contribution of ozone from the stratosphere and ozone produced from naturally emitted precursors is also uncertain. Resolution of the reasons for elevated ozone concentrations in these air masses is needed since the levels are greater than the federal ambient air quality standard.

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